A Summary of the 2005 TMDL Monitoring for Selected Pesticides in the Northern San Joaquin Basin, California

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Introduction

This report describes the results of pesticide monitoring at six locations in four waterways of California's southern Central Valley associated with irrigation runoff that occurred during the months of March, June, July and August of 2005. The river loading rates of diazinon and chlorpyrifos were also calculated for each sampling event. Monitoring was conducted by staff of the Aquatic Ecosystems Analysis Laboratory (AEAL) of the John Muir Institute of the Environment, University of California, Davis, as authorized under Contract No. 02-210-150 from the Central Valley Regional Water Quality Control Board (CVRWQCB).

Objective

The primary objective of this project was to monitor six sites in the northern San Joaquin River basin during the 2005 irrigation season to characterize the sources of diazinon, chlorpyrifos and other pesticides that can cause surface water contamination and toxic conditions to aquatic life. The results of this study will be used to support the development of diazinon and chlorpyrifos TMDLs in the northern San Joaquin basin.

Monitoring Overview

Four sites (Figure 1, Table 1) were monitored weekly for a total of fifteen times each during the following periods: 10-31 March and 29 June - 31 August 2005. Two additional sites on the San Joaquin River (at Patterson and at Lander Avenue) were sampled on alternate weeks during the same time periods. No sampling was conducted during the months April through late-June, because previous monitoring results, and the California Department of Pesticide Regulation pesticide use records, indicate that relatively little diazinon and chlorpyrifos are applied to crops in the northern San Joaquin Basin during these months.

The measured field parameters included pH, water temperature and electrical conductivity (EC). Discharge measurements for selected sites were obtained from U.S. Geological Survey (USGS) and California Department of Water Resources (DWR) data

(Table 2) available on the internet. Water samples were delivered to the California Department of Food and Agriculture (CDFA) laboratory in Sacramento, California for chemical analysis using gas chromatography (GC) and mass spectrometry (MS).

The CDFA laboratory analyzed 12 chemical compounds for each water sample. The list of compounds is provided in Table 3. The detection frequencies, concentrations and calculated instantaneous loading rates for diazinon and chlorpyrifos are presented in Table 5. The detection frequencies and concentrations of the other 10 compounds are listed in Appendix A. The analytical results for all tested compounds, and the physical parameters measured in the field are presented in tabular format on a compact disc appended to this report.

Figure 1. The six sampling sites in the San Joaquin Basin monitored for pesticides during the irrigation season 2005.

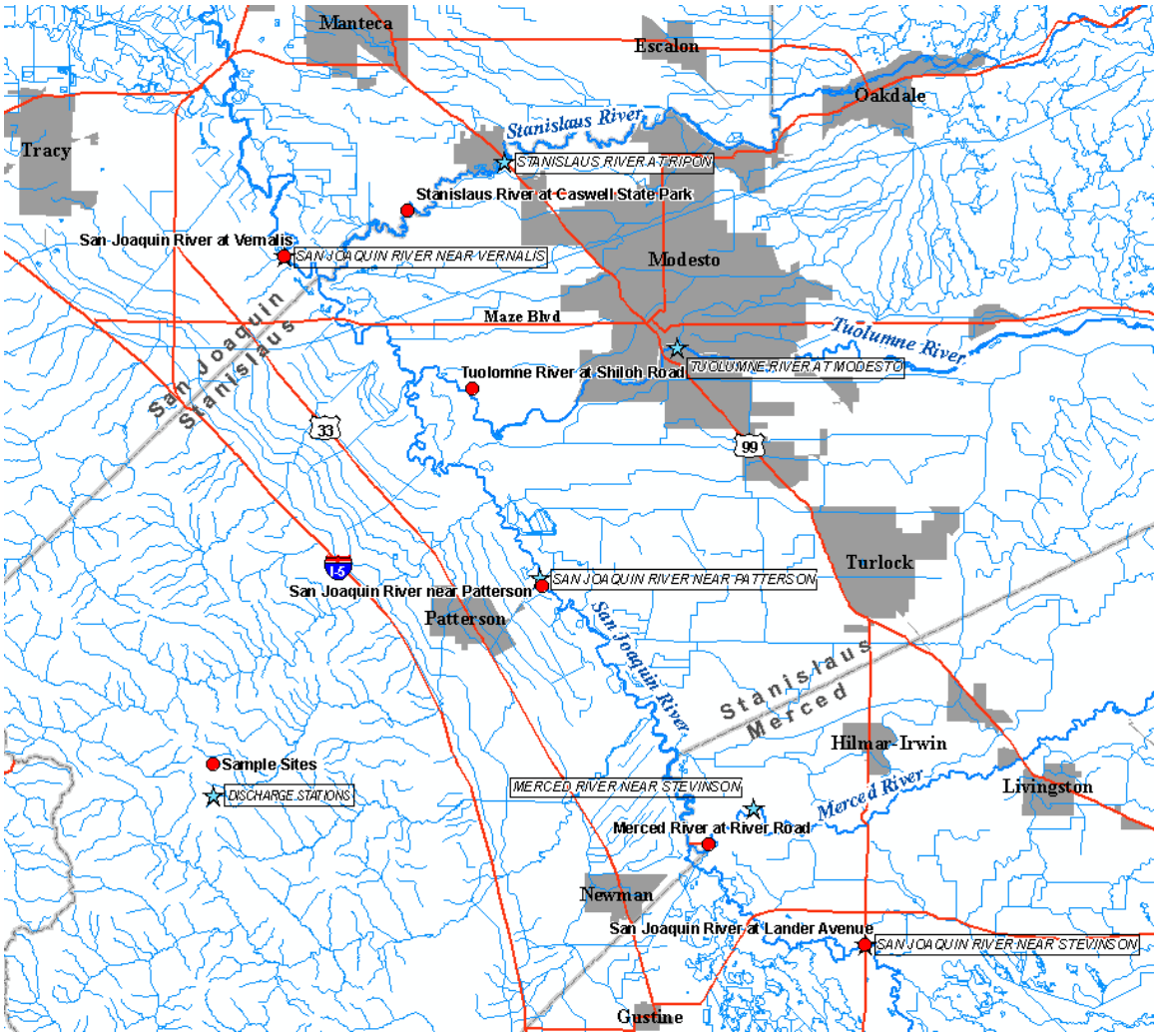

Table 1. Sample sites, collection methods and sampling dates

Site #	Site Name	Sample collection Method	Sampling Dates
1	Merced River at River Road	Integrated grab from bridge	March 10, 17, 22, 31, 2005 June 29, 2005 July 6, 13, 21, 28, 2005 August 3, 10, 17, 24, 31, 2005
5	Tuolumne River at Shiloh Road	Integrated grab from bridge	March 10, 17, 22, 31, 2005 June 29, 2005 July 6, 13, 21, 28, 2005 August 3, 10, 17, 24, 31, 2005
6	San Joaquin River at Vernalis	Integrated grab from bridge	March 10, 17, 22, 31, 2005 June 29, 2005 July 6, 13, 21, 28, 2005 August 3, 10, 17, 24, 31, 2005
7	Stanislaus River at Caswell State Park	Grab from bank	March 10, 17, 22, 31, 2005 June 29, 2005 July 6, 13, 21, 28, 2005 August 3, 10, 17, 24, 31, 2005
13	San Joaquin River at Lander Avenue	Grab from bank	March 10, 22, 2005, June 29, 2005 July 13, 28, 2005 August 10, 24, 2005
14	San Joaquin River at Patterson	Grab from bank	March 17, 31, 2005 July 6, 21, 2005 August 3, 17, 31, 2005

Sample Collection Methods

All samples were collected by either grab or integrated grab methods (Table 1).

Grab samples were collected by harnessing a 1-liter amber glass bottle to a pole sampler and dipping the bottle into the stream as close to the center of the channel as possible.

Integrated grab samples were collected by lowering a 3-liter PTFE (polytetrafluoroethylene) bottle, strapped in a weighted cage, from a bridge at three equally spaced verticals. At each vertical the bottle was filled approximately ¼ full. The composite sample was then thoroughly agitated and poured into a 1-liter amber glass sample bottle.

Discharge Sources, Methods and Stream Drainage Characteristics

Discharge estimates were obtained from USGS and DWR gages listed on the California Data Exchange Center (CDEC) http://cdec.water.ca.gov/ website. At sites where discharge gages were not present, discharge values from the nearest gage on the

same stream were used. An explanation of the discharge source and characteristics of the stream drainage are listed below for each site.

Merced River at River Road – Data for this site were obtained from the CDEC gage MST (Merced River at Stevinson) located approximately 3.68 miles upstream. The gage elevation is 59 feet and the sample site elevation is 53 feet. The low gradient (6 feet over 3.68 miles) and the size of the river allowed us to make the assumption that the river rises fairly uniformly under normal conditions, therefore, flow data from the MST gage were used unadjusted. There is one semi-permanent stream between the sample site and the discharge gage. Flows are unknown for this stream and were assumed to be negligible. The river flows through an urban area near Livingston about 20 miles upstream from the sample site.

Tuolumne River at Shiloh Road **-** The CDEC gage MOD (Tuolumne River at Modesto) was used to obtain discharge measurements for the sampling site. There are no other suitable gages for making any kind of distance-weighted hydrograph, so the data were used as presented on the CDEC website. There are significant urban areas upstream, including Modesto and Waterford. Since we did not measure discharge at this site, and no other measures were taken to determine the applicability of the MOD discharge data, we cannot draw any conclusions about the accuracy of the discharge estimates.

San Joaquin River at Vernalis – USGS and DWR jointly operated discharge station 11303500 (San Joaquin River near Vernalis) was used for this site. The sampling site and gage are both located at the Durham Ferry highway bridge. Data were used unadjusted from the CDEC website. This location is approximately 2.6 miles downstream of the confluence with the Stanislaus River. The drainage area is approximately 13,536 mi^2 and also incorporates the flows of the Merced and Tuolumne rivers, Orestimba Creek, Del Puerto Creek, Dry Creek and Salt Slough.

Stanislaus River at Caswell State Park - Discharge was obtained from USGS gage 11303000 on the Stanislaus River near Ripon, approximately eight miles upstream of the sampling site. The CDEC data were used unadjusted from the Ripon station. The river flows through an urban area at Ripon and through several urban areas upstream of Ripon.

San Joaquin River at Lander Avenue - Discharge was obtained from the California Department of Water Resources gage (CDEC id: SJS) located at the sampling site approximately 2.25 miles south of Stevinson. There are no significant urban influences within 10 miles of the site. The CDEC data were used unadjusted.

San Joaquin River at Patterson - Discharge was obtained from the California Department of Water Resources gage (CDEC id: SJP) located at the sampling site approximately three miles northeast of Patterson. There are no significant urban influences upstream of the site. The CDEC data were used unadjusted.

Table 2. Sampling Sites Discharge Sources

Site Discharge Information							
Site #	**Site Name**	**USGS ID #**	**CDEC ID #**	**Agency**	**Type**	**Lat**	**Long**
1	Merced River at River Road	---	MST	DWR	Hourly	37°22'16"	120°55'52"
5	Tuolumne River at Shiloh Road	11290000	MOD	USGS/DWR	Hourly	37°37'38"	120°59'11"
6	San Joaquin River at Vernalis	11303500	VNS	USGS	Hourly	37°40'01"	121°16'01"
7	Stanislaus River at Caswell State Park	11303000	RIP	USGS	Hourly	37°43'48"	121°06'32"
13	San Joaquin River at Lander Avenue		SJS	DWR	Hourly	37°17'42"	120°51'04"
14	San Joaquin River at Patterson		SJP	DWR	Hourly	37°29'38"	121°04'51"

Loading Rate Calculations

Instantaneous loading rates of diazinon and chlorpyrifos were calculated by multiplying the stream discharge at the time of sample collection by the measured concentrations of each pesticide by the number of seconds (86,400) in one day. Loading rates were only calculated when the pesticide concentration was above the limit of detection and a discharge estimate was available. For all samples where pesticide concentrations were below the limit of detection, the loading rate was assumed to be zero.

The highest and lowest calculated instantaneous loading rates for diazinon were in Tuolumne River and the Merced River, respectively. The highest and lowest calculated instantaneous loading rates for chlorpyrifos were in the San Joaquin River at Vernalis and the Stanislaus River, respectively.

Laboratory Analysis Methods

Upon arrival at the CDFA laboratory, the environmental samples were weighed then spiked with 500µL of 1.0 µg/ml chlorpyrifos methyl (0.5µg/mL) surrogate spiking solution. Each sample was emptied into a 2-liter separatory funnel and approximately 10-15g of granular sodium chloride was added. Sixty ml of methylene chloride were added and the sample was then mixed for three minutes. The organic fraction was filtered through a bed of granular anhydrous sodium sulfate (approx. 20g). The extraction process was repeated three times and the resultant sample was evaporated to 5-7 ml at 40° C, then evaporated to dryness with an N-evaporator. One ml of methylene chloride and 10µL of a 5.0µg/mL internal standard solution were added to each sample. Samples were stored in a –5ºC freezer until analysis. Samples were analyzed with an Agilent Model 5973 GC-MSD using a HP-5MS or equivalent GC column. Analysis was performed in the selective ion-monitoring mode.

Each samples was analyzed for twelve compounds. The compounds and their respective limits of quantitation (LOQ) and limits of detection (LOD) are listed in Table 3. The lab reported estimated values when the values were below the LOQ but above the LOD. To ensure the accuracy and precision of the sample analysis, lab spikes, blanks, and a surrogate standard (chlorpyrifos methyl) were used. If the recovery of a spike sample was out of the control range, the water sample was re-analyzed.

Table 3. CDFA Laboratory limits of detection and practical quantitation limits for select pesticides

Compound	Limit of Detection (LOD in µg/L)	Limit of Quantitation (LOQ in µg/L)
Azinphos methyl	0.007	0.050
Bifenthrin	0.007	0.050
Carbaryl	0.007	0.020
Chlorpyrifos	0.004	0.010
Cyanazine	0.007	0.050
Dacthal (DCPA)	0.007	0.050
Diazinon	0.007	0.020
EPTC (Eptam)	0.020	0.050
Methidathion	0.010	0.030
Metolachlor	0.007	0.020
Propargite	0.150	0.500
Simazine	0.005	0.200

Quality Assurance Objectives

Sampling during the 2005 irrigation season was conducted under the guidance of the Sacramento, Delta and San Joaquin River Basins Organophosphorus Pesticides TMDL Monitoring Quality Assurance Project Plan (QAPP) (Calanchini, 2005).

Sampling precision and variability are measured through the use of field duplicates and matrix spike duplicates. The Quality Assurance Objective (QAO) for precision was a relative percent difference (RPD) of $\pm$ 25% between duplicate samples and their corresponding environmental samples, and between matrix spike samples and their corresponding matrix spike duplicates (Table 4).

Accuracy is measured by determining the percent recovery of known concentrations of analytes spiked into environmental samples or reagent water before extraction. The QAO for accuracy in laboratory analytical measurements was a 70% - 130% recovery rate of chlorpyrifos and a 70% - 140% recovery rate for diazinon in matrix spike samples, or control limits at $\pm$ 3 standard deviations based on actual lab data, and 80% - 125% in all surrogates (Table 4). Two environmental samples and one quality control sample had surrogate recoveries outside of the QAO acceptance limits – see footnotes in Tables 5 & 6 and Appendix A. All matrix spike samples met the QAO for accuracy (Table 6).

Table 4. Field and Laboratory Quality Assurance (QA) Objectives.

Field QC	**Frequency/Number**	**Acceptance Limits**	**Results (met QAO/total)**
Field Blanks	Approximately 5%	Less than Reporting Limit	12/12
Cooler Temperature	Measured by analyzing lab at time of delivery	$\leq$ 4° C	100%
Field Duplicate Pairs	16	RPD $\leq$ 25%	14/16 chlorpyrifos 15/16 diazinon
Laboratory QC	**Frequency/Number**	**Acceptance Limits**	
Method Blank (=Lab Blank)	1/batch	80-125% All target analytes below reporting limit	14/14
Instrument Blank	After any standards	All target analytes below reporting limit	100%
Matrix Spike	Approximately 5%	70-130 % diazinon; 70-140% chlorpyrifos	4/4 chlorpyrifos 4/4 diazinon
Lab. Control Sample (=Lab Control Spike)	1/Batch	80-125%	14/14
Surrogates	In all samples and QC	80-125%	99/102
Internal Standards	All samples and standards	50 – 200 %	100%

Results

A total of 70 environmental samples (Table 5) and 32 quality control (QC) samples (Table 6) were collected and analyzed.

Environmental samples

Concentrations of diazinon and chlorpyrifos ranged from below detection to 0.013 parts per billion (ppb) of diazinon and 0.025 ppb chlorpyrifos (Table 5).

Other pesticides detected in the environmental samples were EPTC (Eptam), Simazine, Carbaryl, Metolachlor, Propargite and Azinphos-methyl (Appendix A).

Quality Control Samples

Sample quality control was measured through collection of sequential and split duplicates (n=16), field blanks (n=12) and matrix spikes (n=4). Duplicate samples provided a measure of analytical precision; field blanks were used to evaluate possible introduction of contaminants during sample collection, handling and transport to the lab; and matrix spikes were used to evaluate the relative percent recovery of spiked chemicals by the extraction from the sample matrix.

The procedures used for collecting the QA/QC samples were based on the Sacramento, Delta and San Joaquin River Basins Organophosphorus Pesticides TMDL Monitoring Quality Assurance Project Plan (Calanchini, 2005).

The QAO for duplicate samples is a relative percent difference (RPD) of $\leq$ 25% between the duplicate and the corresponding environmental sample concentrations. The RPDs for chlorpyrifos ranged from 0 – 46.15% with two duplicates failing to meet the QAO acceptance limits. Only one duplicate sample had a detection of diazinon. The RPD between that sample and the corresponding environmental sample was 28.57% (Table 6).

Two samples that were scheduled as field blanks were accidentally collected as duplicates. These samples are listed as duplicates in Table 6 and are identified with a footnote.

The QAO acceptance limit for field blanks is “less than the reporting limit”. All twelve field blanks met the acceptance limits, however there was a single detection. The field blank collected on August 31 had a (estimated) detection of 0.005 parts per billion (ppb) of chlorpyrifos. The CDFA Limit of Detection (LOD) and Reporting Limit (RL)

for chlorpyrifos are 0.004 ppb and 0.010 ppb, respectively. Because the detections of chlorpyrifos in the field blank and corresponding environmental sample were both below the RL, and therefore not quantifiable, the samples should be considered as uncontaminated and the results reported without qualifications.

The QAO acceptance limits for matrix spikes were 70-130% for chlorpyrifos and 70-140% for diazinon. All four matrix spikes met the QAO objectives for recovery. Recoveries ranged from 83-98% for chlorpyrifos and 86-108% for diazinon.

A summary of the environmental data is presented in Table 5 and Appendix A. A summary of the lab blank and spike data are presented in Appendices B and C.

Table 5. Summary of environmental data collected on diazinon and chlorpyrifos concentrations and instantaneous loading rates for sites in the San Joaquin River Basin, California. March, July and August 2004.

Stream flow is in cubic feet per second. J: the reported concentrations were below the quantitative limit and are considered estimates; NA: not available; ND: Not detected; g a.i./d: grams active ingredient per day; µg/L: microgram per liter. All samples collected on 28 July 2005 had low initial surrogate recovery and were re-extracted. The re-extracted samples exceeded the seven-day holding period prior to extraction by one day.

Site number	Site name	Site identification number	Date (month/day/year)	Time (24 hr)	Stream flow (cfs)	Chlorpyrifos concentration (µg/L)	Chlorpyrifos instantaneous loading rate (g a.i./d)	Diazinon concentration (µg/L)	Diazinon instantaneous loading rate (g a.i./d)
1	Merced R @ River Rd	11273500	3/10/2005	10:40	287	0.014	9.83	ND	NA
			3/17/2005	9:50	239	ND	NA	ND	NA
			3/22/2005	10:10	295	(0.008 J)	5.77	(0.008 J)	5.77
			3/31/2005	9:50	4817	ND	NA	ND	NA
			6/29/2005	10:10	908	ND	NA	ND	NA
			7/6/2005	9:40	1062	(0.005 J)	12.99	ND	NA
			7/13/2005	10:00	697	(0.007 J)	11.94	ND	NA
			7/21/2005	9:40	497	0.016	19.45	ND	NA
			7/28/2005	10:40	625	(0.004 J)	6.12	ND	NA
			8/3/2005	10:30	559	ND	NA	ND	NA
			8/10/2005	10:30	681	0.018	29.99	ND	NA
			8/17/2005	10:50	762	ND	NA	ND	NA
			8/24/2005	10:30	924	(0.007 J)	15.82	ND	NA
			8/31/2005	10:40	497	ND	NA	ND	NA
5	Tuolumne River at Shiloh Road	11290000	3/10/2005	11:30	3990	ND	NA	ND	NA
			3/17/2005	11:50	3700	ND	NA	(0.013 J)	117.68
			3/22/2005	11:20	3585	ND	NA	ND	NA
			3/31/2005	11:10	6390	ND	NA	ND	NA
			6/29/2005	11:00	2900	ND	NA	ND	NA
			7/6/2005	11:00	3650	ND	NA	ND	NA
			7/13/2005	10:50	1970	0.012	57.84	ND	NA
			7/21/2005	10:30	1680	0.022	90.42	ND	NA
			7/28/2005	11:50	1590	(0.006 J)	23.34	ND	NA
			8/3/2005[1]	11:40	1500	(0.006 J)	22.02	ND	NA
			8/10/2005	11:20	1240	0.011	33.37	ND	NA
			8/17/2005	12:10	1220	0.014	41.79	(0.008 J)	NA

Table 5. Summary of environmental data collected on diazinon and chlorpyrifos concentrations and instantaneous loading rates for sites in the San Joaquin River Basin, California. March, July and August 2004.

Stream flow is in cubic feet per second. J: the reported concentrations were below the quantitative limit and are considered estimates; NA: not available; ND: Not detected; g a.i./d: grams active ingredient per day; µg/L: microgram per liter. All samples collected on 28 July 2005 had low initial surrogate recovery and were re-extracted. The re-extracted samples exceeded the seven-day holding period prior to extraction by one day.

Site number	Site name	Site identification number	Date (month/day/year)	Time (24 hr)	Stream flow (cfs)	Chlorpyrifos concentration (µg/L)	Chlorpyrifos instantaneous loading rate (g a.i./d)	Diazinon concentration (µg/L)	Diazinon instantaneous loading rate (g a.i./d)
5	Tuolumne River at Shiloh Road	11290000	8/24/2005	11:50	899	(0.007 J)	15.40	ND	NA
	continued		8/31/2005	12:00	511	ND	NA	ND	NA
6	San Joaquin River at Vernalis	11303500	3/10/2005	12:00	6800	0.011	183.00	ND	NA
			3/17/2005	12:20	6040	ND	NA	ND	NA
			3/22/2005	12:00	5840	(0.006 J)	85.73	ND	NA
			3/31/2005	11:50	14400	(0.004 J)	140.92	ND	NA
			6/29/2005	11:50	6020	ND	NA	ND	NA
			7/6/2005	11:30	7050	(0.009 J)	155.23	ND	NA
			7/13/2005	11:30	4820	0.014	165.09	ND	NA
			7/21/2005	11:20	3860	0.012	113.32	ND	NA
			7/28/2005	12:30	3450	(0.007 J)	59.08	ND	NA
			8/3/2005	12:30	3340	0.011	89.88	ND	NA
			8/10/2005	12:00	2680	(0.010 J)	65.57	ND	NA
			8/17/2005	12:50	2690	(0.010 J)	65.81	ND	NA
			8/24/2005	12:30	2540	0.015	93.21	ND	NA
			8/31/2005	12:20	1980	(0.007 J)	33.91	ND	NA
7	Stanislaus River at Caswell S.P.	374209121103800	3/10/2005	12:50	284	(0.007 J)	4.86	ND	NA
			3/17/2005	12:50	271	(0.005 J)	3.32	ND	NA
			3/22/2005	12:40	352	(0.008 J)	6.89	(0.012 J)	10.33
			3/31/2005	12:30	609	ND	NA	ND	NA
			6/29/2005	12:20	315	ND	NA	ND	NA
			7/6/2005	12:10	296	0.013	9.41	ND	NA
			7/13/2005	12:10	341	0.019	15.85	ND	NA
			7/21/2005	12:00	346	0.014	11.85	ND	NA
			7/28/2005	13:00	324	0.014	11.10	ND	NA
			8/3/2005	13:00	306	(0.010 J)	7.49	ND	NA
			8/10/2005	12:30	288	ND	NA	ND	NA

Table 5. Summary of environmental data collected on diazinon and chlorpyrifos concentrations and instantaneous loading rates for sites in the San Joaquin River Basin, California. March, July and August 2004.

Stream flow is in cubic feet per second. J: the reported concentrations were below the quantitative limit and are considered estimates; NA: not available; ND: Not detected; g a.i./d: grams active ingredient per day; µg/L: microgram per liter. All samples collected on 28 July 2005 had low initial surrogate recovery and were re-extracted. The re-extracted samples exceeded the seven-day holding period prior to extraction by one day.

Site number	Site name	Site identification number	Date (month/day/year)	Time (24 hr)	Stream flow (cfs)	Chlorpyrifos concentration (µg/L)	Chlorpyrifos instantaneous loading rate (g a.i./d)	Diazinon concentration (µg/L)	Diazinon instantaneous loading rate (g a.i./d)
7	Stanislaus River at Caswell S.P.	374209121103800	8/17/2005	13:20	295	0.013	9.38	ND	NA
	continued		8/24/2005	13:00	288	ND	NA	ND	NA
			8/31/2005	12:50	309	0.025	18.90	ND	NA
13	San Joaquin River at Lander Avenue	11260815	3/10/2005	10:00	724	(0.008 J)	14.17	(0.008 J)	14.17
			3/22/2005	9:30	1083	(0.006 J)	15.90	ND	NA
			6/29/2005	9:30	722	ND	NA	ND	NA
			7/13/2005	9:40	52	(0.006 J)	0.76	ND	NA
			7/28/2005	10:20	16	ND	NA	ND	NA
			8/10/2005	10:00	62	0.025	3.79	ND	NA
			8/24/2005	10:10	63	ND	NA	ND	NA
14	San Joaquin River at Patterson	11274570	3/17/2005	10:30	1198	0.012	35.17	ND	NA
			3/31/2005	10:40	8570	(0.007 J)	146.77	ND	NA
			7/6/2005	10:30	1681	0.01	41.13	ND	NA
			7/21/2005	10:10	1056	0.017	43.92	ND	NA
			8/3/2005[2]	11:10	824	(0.008 J)	16.13	ND	NA
			8/17/2005	11:30	1152	0.011	31.00	ND	NA
			8/31/2005	11:20	848	(0.007 J)	14.52	ND	NA

[1]Surrogate recovery (73%) was outside of QAPP acceptance limits. Results should be viewed as biased low.

[2]Surrogate recovery (68%) was outside of QAPP acceptance limits. Results should be viewed as biased low.

Table 6. Summary of diazinon and chlorpyrifos concentrations quality-control data for sites in the San Joaquin River Basin, California, March, June, July and August 2005.

NA: not applicable - cannot be calculated because of "less than" concentration; µg/L: microgram per liter; J: the reported concentrations were below the quantitative limit and are considered estimates; <: less than

Site identification number	Site name	Date and time (month/day/year 24-hour time)	Chlorpyrifos (ug/L)	Relative percent difference OR percent recovery (chlorpyrifos)	Diazinon (ug/L)	Relative percent difference OR percent recovery (diazinon)
DUPLICATES[1]						
11273500	Merced River at River Road	3/17/2005 9:50	<0.004		<0.007	
		3/17/2005 9:53	(0.004 J)	NA	<0.007	NA
11273500	Merced River at River Road	7/6/2005 9:40	(0.005 J)		<0.007	
		7/6/2005 9:43	(0.007 J)	33.33%	<0.007	NA
11273500	Merced River at River Road	8/3/2005 10:30	<0.004		<0.007	
		8/3/2005 10:33	<0.004	NA	<0.007	NA
11273500	Merced River at River Road	8/31/2005 10:40	<0.004		<0.007	
		8/31/2005 10:43	<0.004	NA	<0.007	NA
11290200	Tuolumne River at Shiloh Road	6/29/2005 11:00	<0.004		<0.007	
		6/29/2005 11:03	<0.004	NA	<0.007	NA
11290200	Tuolumne River at Shiloh Road	7/28/2005 11:50	(0.006 J)[3]		<0.007	
		7/28/2005 11:53	<0.004	NA	<0.007	NA
11290200	Tuolumne River at Shiloh Road	8/24/2005 11:50	(0.007 J)		<0.007	
		8/24/2005 11:53	(0.006 J)	15.38%	<0.007	NA
11303500	San Joaquin River at Vernalis	3/10/2005 12:00	0.011		<0.007	
		3/10/2005 12:03	0.011	0%	<0.007	NA
11303500	San Joaquin River at Vernalis	8/10/2005 11:50	(0.010 J)		<0.007	
		8/10/2005 11:51[2]	0.012	18.18%	<0.007	NA
374209121103800	Stanislaus River at Caswell State Park	3/22/2005 12:40	(0.008 J)		(0.012 J)	
		3/22/2005 12:43	(0.005 J)	46.15%	(0.009 J)	28.57%
374209121103800	Stanislaus River at Caswell State Park	7/13/2005 12:10	0.019		<0.007	
		7/13/2005 12:13	0.021	10.00%	<0.007	NA
374209121103800	Stanislaus River at Caswell State Park	8/10/2005 12:30	<0.004		<0.007	
		8/10/2005 12:33	<0.004	NA	<0.007	NA
11274570	San Joaquin River at Patterson	3/17/2005 10:30	0.012		<0.007	
		3/17/2005 10:31[2]	0.011	8.70%	<0.007	NA
11274570	San Joaquin River at Patterson	3/31/2005 10:40	(0.007 J)		<0.007	
		3/31/2005 10:43	(0.007 J)	0%	<0.007	NA
11274570	San Joaquin River at Patterson	7/21/2005 10:10	0.017		<0.007	
		7/21/2005 10:13	0.016	6.06%	<0.007	NA
11274570	San Joaquin River at Patterson	8/17/2005 11:30	0.011		<0.007	
		8/17/2005 11:33	0.017	42.86%	<0.007	NA
BLANKS						
11290200	Tuolumne River at Shiloh Road	3/10/2005 11:31	<0.004		<0.007	
11290200	Tuolumne River at Shiloh Road	3/31/2005 11:11	<0.004		<0.007	

Table 6. Summary of diazinon and chlorpyrifos concentrations quality-control data for sites in the San Joaquin River Basin, California, March, June, July and August 2005.

NA: not applicable - cannot be calculated because of "less than" concentration; µg/L: microgram per liter; J: the reported concentrations were below the quantitative limit and are considered estimates; <: less than

Site identification number	Site name	Date and time (month/day/year 24-hour time)	Chlorpyrifos (ug/L)	Relative percent difference OR percent recovery (chlorpyrifos)	Diazinon (ug/L)	Relative percent difference OR percent recovery (diazinon)
BLANKS *cont.*						
11290200	Tuolumne River at Shiloh Road	7/21/2005 10:31	<0.004		<0.007	
11290200	Tuolumne River at Shiloh Road	8/17/2005 12:11	<0.004		<0.007	
11303500	San Joaquin River at Vernalis	3/22/2005 12:01	<0.004		<0.007	
11303500	San Joaquin River at Vernalis	6/29/2005 11:51	<0.004		<0.007	
11303500	San Joaquin River at Vernalis	7/13/2005 11:31	<0.004		<0.007	
11303500	San Joaquin River at Vernalis	7/28/2005 12:31	<0.004		<0.007	
11303500	San Joaquin River at Vernalis	8/24/2005 12:31	<0.004		<0.007	
11274570	San Joaquin River at Patterson	7/6/2005 10:31	<0.004		<0.007	
11274570	San Joaquin River at Patterson	8/3/2005 11:11[6]	<0.004		<0.007	
11274570	San Joaquin River at Patterson	8/31/2005 11:21	(0.005 J)		<0.007	
SPIKES[4,5]						
11273500	Merced River at River Road	8/31/05 10:40 8/31/05 10:49	<0.004	90%	<0.007	93%
11290200	Tuolumne River at Shiloh Road	8/24/2005 11:50 8/24/2005 11:59	(0.007 J)	98%	<0.007	108%
11303500	San Joaquin River at Vernalis	8/24/2005 12:30 8/24/2005 12:39	0.015	94%	<0.007	107%
374209121103800	Stanislaus River at Caswell State Park	8/31/2005 12:50 8/31/2005 12:59	0.025	83%	<0.007	86%

[1] Sequential duplicates collected at Stanislaus River at Caswell S.P and San Joaquin River at Patterson; all other sites were split duplicates.
[2] Sample was scheduled as an environmental blank but accidentally collected as a duplicate.
[3] Sample hold time for extraction was exceeded.
[4] Spiked samples were injected with 0.05 ug/L of chlorpyrifos; 0.10 ug/L of diazinon.
[5] First sample in each pair is the environmental sample; second sample is the spike.
[6] Surrogate recovery (60%) was outside of QAPP acceptance limits. Results should be viewed as biased low.

Sources Cited

Calanchini, H. 2005. Sacramento, Delta and San Joaquin River Basins Organophosphorus Pesticides TMDL Monitoring Quality Assurance Project Plan.

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Appendix A

Appendix A. Pesticide results (excluding diazinon and chlorpyrifos).

(Concentrations are in units of µg/L. ND: Not detected; J: the reported concentrations were below the quantitative limit and are considered estimates; All samples collected on 28 July 2005 had low initial surrogate recovery and were re-extracted. The re-extracted samples exceeded the seven-day holding period prior to extraction by one day. Each sample was also analyzed for Bifenthrin[1], Cyanazine, Dacthal (DCPA) and Methidathion which were not present at detectable levels).

Site	Date	Time	EPTC (Eptam)	Simazine	Carbaryl	Metolachlor	Propargite	Azinphos methyl
Merced River at River Rd.	3/10/2005	10:40	ND	(0.026 J)	ND	ND	ND	ND
Merced River at River Rd.	3/17/2005	9:50	ND	(0.011 J)	ND	ND	ND	ND
Merced River at River Rd.	3/22/2005	10:10	ND	(0.026 J)	ND	ND	ND	ND
Merced River at River Rd.	3/31/2005	9:50	ND	(0.031 J)	ND	ND	ND	ND
Merced River at River Rd.	6/29/2005	10:10	ND	ND	ND	ND	ND	ND
Merced River at River Rd.	7/6/2005	9:40	ND	ND	ND	ND	ND	ND
Merced River at River Rd.	7/13/2005	10:00	ND	ND	ND	ND	ND	ND
Merced River at River Rd.	7/21/2005	9:40	ND	ND	ND	ND	ND	ND
Merced River at River Rd.	7/28/2005	10:40	ND	ND	(0.012 J)	ND	ND	ND
Merced River at River Rd.	8/3/2005	10:30	ND	ND	ND	ND	ND	ND
Merced River at River Rd.	8/10/2005	10:30	ND	(0.160 J)	ND	(0.016 J)	ND	ND
Merced River at River Rd.	8/17/2005	10:50	ND	ND	ND	ND	ND	ND
Merced River at River Rd.	8/24/2005	10:30	ND	ND	ND	ND	ND	ND
Merced River at River Rd.	8/31/2005	10:40	ND	ND	ND	ND	ND	ND
Tuolumne River at Shiloh Rd.	3/10/2005	11:30	ND	(0.023 J)	ND	ND	ND	ND
Tuolumne River at Shiloh Rd.	3/17/2005	11:50	ND	(0.018 J)	ND	ND	ND	ND
Tuolumne River at Shiloh Rd.	3/22/2005	11:20	ND	(0.020 J)	ND	ND	ND	ND
Tuolumne River at Shiloh Rd.	3/31/2005	11:10	ND	(0.024 J)	ND	ND	ND	ND
Tuolumne River at Shiloh Rd.	6/29/2005	11:00	ND	(0.017 J)	ND	ND	ND	ND
Tuolumne River at Shiloh Rd.	7/6/2005	11:00	ND	(0.017 J)	ND	ND	ND	ND
Tuolumne River at Shiloh Rd.	7/13/2005	10:50	ND	(0.014 J)	ND	ND	ND	ND
Tuolumne River at Shiloh Rd.	7/21/2005	10:30	ND	(0.013 J)	ND	ND	ND	ND

[1] Analysis for bifenthrin was discontinued after the July 28 sampling event.

Appendix A. Pesticide results (excluding diazinon and chlorpyrifos).

(Concentrations are in units of µg/L. ND: Not detected; J: the reported concentrations were below the quantitative limit and are considered estimates; All samples collected on 28 July 2005 had low initial surrogate recovery and were re-extracted. The re-extracted samples exceeded the seven-day holding period prior to extraction by one day. Each sample was also analyzed for Bifenthrin[1], Cyanazine, Dacthal (DCPA) and Methidathion which were not present at detectable levels).

Site	Date	Time	EPTC (Eptam)	Simazine	Carbaryl	Metolachlor	Propargite	Azinphos methyl
Tuolumne River at Shiloh Rd.	7/28/2005	11:50	ND	(0.012 J)	ND	ND	ND	ND
Tuolumne River at Shiloh Rd.	8/3/2005[2]	11:40	ND	(0.011 J)	ND	ND	ND	ND
Tuolumne River at Shiloh Rd.	8/10/2005	11:20	ND	(0.010 J)	ND	ND	ND	ND
Tuolumne River at Shiloh Rd.	8/17/2005	12:10	ND	(0.013 J)	ND	ND	ND	ND
Tuolumne River at Shiloh Rd.	8/24/2005	11:50	ND	(0.011 J)	ND	ND	ND	ND
Tuolumne River at Shiloh Rd.	8/31/2005	12:00	ND	(0.009 J)	ND	ND	ND	ND
San Joaquin River at Vernalis	3/10/2005	12:00	ND	(0.044 J)	ND	(0.009 J)	ND	ND
San Joaquin River at Vernalis	3/17/2005	12:20	ND	(0.190 J)	ND	ND	ND	ND
San Joaquin River at Vernalis	3/22/2005	12:00	ND	(0.040 J)	ND	ND	ND	ND
San Joaquin River at Vernalis	3/31/2005	11:50	ND	(0.038 J)	ND	ND	ND	ND
San Joaquin River at Vernalis	6/29/2005	11:50	ND	(0.012 J)	ND	0.057	ND	ND
San Joaquin River at Vernalis	7/6/2005	11:30	ND	(0.012 J)	ND	0.046	ND	ND
San Joaquin River at Vernalis	7/13/2005	11:30	ND	(0.010 J)	ND	0.140	ND	ND
San Joaquin River at Vernalis	7/21/2005	11:20	ND	(0.012 J)	ND	0.160	ND	ND
San Joaquin River at Vernalis	7/28/2005	12:30	ND	(0.010 J)	ND	0.180	ND	ND
San Joaquin River at Vernalis	8/3/2005	12:30	ND	(0.008 J)	ND	0.100	ND	ND
San Joaquin River at Vernalis	8/10/2005	12:00	ND	(0.011 J)	ND	0.100	ND	ND
San Joaquin River at Vernalis	8/17/2005	12:50	ND	(0.009 J)	ND	0.068	ND	ND
San Joaquin River at Vernalis	8/24/2005	12:30	ND	ND	ND	0.060	ND	ND
San Joaquin River at Vernalis	8/31/2005	12:20	ND	(0.010 J)	ND	0.040	ND	ND
Stanislaus River at Caswell State Park	3/10/2005	12:50	ND	0.240	ND	ND	ND	ND
Stanislaus River at Caswell State Park	3/17/2005	12:50	ND	(0.026 J)	ND	ND	ND	ND

[2] Surrogate recovery (73%) was outside of QAPP acceptance limits. Results should be viewed as biased low.

Appendix A. Pesticide results (excluding diazinon and chlorpyrifos).

(Concentrations are in units of µg/L. ND: Not detected; J: the reported concentrations were below the quantitative limit and are considered estimates; All samples collected on 28 July 2005 had low initial surrogate recovery and were re-extracted. The re-extracted samples exceeded the seven-day holding period prior to extraction by one day. Each sample was also analyzed for Bifenthrin[1], Cyanazine, Dacthal (DCPA) and Methidathion which were not present at detectable levels).

Site	Date	Time	EPTC (Eptam)	Simazine	Carbaryl	Metolachlor	Propargite	Azinphos methyl
Stanislaus River at Caswell State Park	3/22/2005	12:40	ND	0.250	0.029	ND	ND	ND
Stanislaus River at Caswell State Park	3/31/2005	12:30	ND	0.270	ND	ND	ND	ND
Stanislaus River at Caswell State Park	6/29/2005	12:20	ND	ND	ND	ND	ND	ND
Stanislaus River at Caswell State Park	7/6/2005	12:10	ND	(0.013 J)	ND	ND	ND	ND
Stanislaus River at Caswell State Park	7/13/2005	12:10	ND	(0.011 J)	ND	ND	ND	ND
Stanislaus River at Caswell State Park	7/21/2005	12:00	0.051	(0.010 J)	(0.007 J)	ND	ND	ND
Stanislaus River at Caswell State Park	7/28/2005	13:00	ND	(0.010 J)	ND	ND	ND	ND
Stanislaus River at Caswell State Park	8/3/2005	13:00	ND	(0.011 J)	ND	ND	ND	ND
Stanislaus River at Caswell State Park	8/10/2005	12:30	ND	(0.011 J)	ND	ND	ND	ND
Stanislaus River at Caswell State Park	8/17/2005	13:20	ND	(0.010 J)	ND	ND	ND	ND
Stanislaus River at Caswell State Park	8/24/2005	13:00	ND	(0.010 J)	ND	ND	ND	ND
Stanislaus River at Caswell State Park	8/31/2005	12:50	ND	(0.010 J)	ND	ND	ND	ND
San Joaquin River at Lander Avenue	3/10/2005	10:00	ND	(0.016 J)	ND	0.046	ND	ND
San Joaquin River at Lander Avenue	3/22/2005	9:30	ND	(0.007 J)	ND	ND	ND	ND
San Joaquin River at Lander Avenue	6/29/2005	9:30	ND	ND	ND	0.089	ND	ND
San Joaquin River at Lander Avenue	7/13/2005	9:40	ND	(0.039 J)	ND	1.600	ND	ND
San Joaquin River at Lander Avenue	7/28/2005	10:20	ND	ND	ND	4.000[3]	ND	ND
San Joaquin River at Lander Avenue	8/10/2005	10:00	ND	(0.170 J)	ND	(0.013 J)	(0.18 J)	0.780[4]
San Joaquin River at Lander Avenue	8/24/2005	10:10	(0.028 J)	ND	ND	0.680[5]	ND	ND
San Joaquin River at Patterson	3/17/2005	10:30	ND	(0.026 J)	ND	(0.012 J)	ND	ND
San Joaquin River at Patterson	3/31/2005	10:40	ND	(0.022 J)	ND	ND	ND	ND

[3] 1/20 dilution

[4] ¼ dilution

[5] ½ dilution

Appendix A. Pesticide results (excluding diazinon and chlorpyrifos).

(Concentrations are in units of µg/L. ND: Not detected; J: the reported concentrations were below the quantitative limit and are considered estimates; All samples collected on 28 July 2005 had low initial surrogate recovery and were re-extracted. The re-extracted samples exceeded the seven-day holding period prior to extraction by one day. Each sample was also analyzed for Bifenthrin[1], Cyanazine, Dacthal (DCPA) and Methidathion which were not present at detectable levels).

Site	Date	Time	EPTC (Eptam)	Simazine	Carbaryl	Metolachlor	Propargite	Azinphos methyl
San Joaquin River at Patterson	7/6/2005	10:30	0.062	(0.005 J)	ND	0.140	ND	ND
San Joaquin River at Patterson	7/21/2005	10:10	ND	(0.007 J)	(0.018 J)	0.350	ND	ND
San Joaquin River at Patterson	8/3/2005	11:10	ND	ND	ND	0.220	(0.150 J)	ND
San Joaquin River at Patterson	8/17/2005	11:30	0.094	(0.006 J)	ND	0.140	(0.250 J)	ND
San Joaquin River at Patterson	8/31/2005[6]	11:20	ND	ND	ND	0.076	ND	ND

[6] Surrogate recovery (68%) was outside of QAPP acceptance limits. Results should be viewed as biased low.

Appendix B. Lab Blank Data

(No pesticides were present at detectable levels. The pesticides include azinphos methyl, bifenthrin, carbaryl, chlorpyrifos, cyanazine, diazinon, dacthal (DCPA), EPTC (Eptam), metolachlor, methidathion, propargite, simazine)

Date Extracted	Chlorpyrifos Methyl (Surrogate) Recovery
3/15/2005	88%
3/22/2005	81%
3/24/2005	100%
4/5/2005	81%
7/5/2005	111%
7/11/2005	80%
7/18/2005	90%
7/22/2005	91%
8/5/2005*	102%
8/5/2005	85%
8/15/2005	81%
8/18/2005	87%
8/26/2005	91%
9/6/2005	94%

* Associated samples (collected 7/28/2005) had low surrogate recovery. Samples were re-extracted eight days after collection exceeding seven-day hold time specified in QAPP.

Appendix C. Recovery of lab spikes and surrogates

Date Extracted	Diazinon	Chlorpyrifos	Surrogate
3/15/2005	105%	101%	97%
3/22/2005	102%	88%	93%
3/24/2005	104%	98%	96%
4/5/2005	104%	100%	94%
7/5/2005	88%	114%	106%
7/11/2005	103%	101%	106%
7/18/2005	83%	88%	80%
7/22/2005	99%	87%	87%
8/5/2005*	98%	88%	94%
8/5/2005	122%	113%	116%
8/15/2005	101%	94%	94%
8/18/2005	112%	93%	96%
8/26/2005	93%	83%	93%
9/6/2005	95%	94%	92%

* Associated samples (collected 7/28/2005) had low surrogate recovery. Samples were re-extracted eight days after collection exceeding seven-day hold time specified in QAPP.